16086

Complex Processes in Electrochemical Systems

Henry A. Catherino
U.S. Army Research Development and Engineering Command
AMSRD-TAR-R/MS 121
Warren, MI 49397-5000

catherih@tacom.army.mil

Keywords: batteries, complexity, electrochemistry, non-linearity

Abstract

The study of the individual components comprising a physical system is a necessary first step for understanding the behavior of the system. However, when the individual components are brought together, unexpected consequences have a way of taking place that were not anticipated by the studies on the individual components. This is usually the consequence of the union of components that comprise a non-linear system. The term "non-linear" is understood within the usual analytical definition: [4]

$$f(a+b) = f(a) + f(b) \qquad (1)$$

and

$$cf(b) = f(cb) \qquad (2)$$

For present purposes, it is equation (1) that is of interest. In it lies a fundamental facet of human thinking. Simply put, equation (1) states that if a problem is divided into it parts and the parts are studied independently, then the parts can be reassembled and the response of the union can be predicted. This sometimes works. One name that characterizes this kind of behavior is the Principle of Superposition which is found in the analysis of electrical circuits. The nice thing about linearity is that the problems tend to have computable solutions. Another nice thing is that the systems being described can be easily categorized into discrete and unique parts and the mathematics is simpler and solutions exist.

Non-linearity requires terms not included in equation (1) that suggest the existence of interactions between the components. The feedback between the components has a way of making the cause and effect presumption to become fuzzy. This is what characterizes a complex process.

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE **01 AUG 2006**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**

4. TITLE AND SUBTITLE **Complex Processes in Electrochemical Systems**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Henry A. Catherino**	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **US ARMY TACOM 6501 E 11 Mile Road Warren, MI 48397-5000**	8. PERFORMING ORGANIZATION REPORT NUMBER **16086**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) **TACOM TARDEC** 11. SPONSOR/MONITOR'S REPORT NUMBER(S) **16086**

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**SAR**	**8**	

Electrochemical systems are an example of the union of non-linear components. They show the effects of (1) sensitive dependence on initial conditions, (2) self-organizing behavior and (3) chaotic oscillations. The study described in this paper illustrates examples of this complex behavior and suggests that understanding the strange behaviors can be assisted by analyzing them as dynamical systems. The interactions between the electrolyte and the active materials in the cell can be surprising and remarkable.

Introduction

An ever present activity is the continuing effort to model the behavior of engineered systems. The hope is that the model will allow a prediction of consequent behavior based on a supplied set of input variables. To provide the basis for developing a physical model to predict battery behavior, a vast literature is available that gives detailed descriptions of the fundamental electrochemical processes taking place within an electrochemical cell.[1] To date, the best models are those that limit themselves to narrow operating domains of input variables.[2] It is a fair question to inquire as to why better progress has not already been made in this area.

Intuitively, the usual approach is to divide a problem into discrete parts, characterize the parts and then put the parts together to achieve the desired system wide model. It is also noteworthy that the lead acid battery, as a system, has been around for about 145 years and research work is still ongoing. It is again, reasonable to ask why this is so and why is the model for its behavior still an elusive objective.

Discussion

In the pursuit of a model, it is necessary to define the things that we are interested in talking about. Definitions are characterized as being either descriptive or essential.[3] This is important because the distinction helps to indicate the level of progress that is made in any discipline. The first is the descriptive definition. Definitions of this type define an event or observation in words that are basically a restatement of that which was observed. Actually a classification has taken place. Definitions of this kind are the first steps toward developing a basis for understanding. A property of the descriptive definition is that one usually gets universal agreement using such a definition. The second definition is the essential definition. This definition can include the mechanism by which a process takes place. Mechanistic interpretations are usually mental constructs. Since there can be many alternative ways to interpret a limited set of observed data, the mechanistic definition can result in considerable debate as many points of view exist. However, the mechanistic interpretation has one major redeeming feature; a mechanistic interpretation has a predictive characteristic. Through the use of physical models, quantitative predictions can be made that lead to unprecedented discoveries.

By analytically formulating mechanistic models, it is possible to attempt to develop models of assemblages of multi-component systems, such as a battery. Generating such mathematical models and computing the prediction is relatively easily done provided that the models are linear.

Complexity, Linearity and Non-linearity

The basic description of a linear system is that it conforms to the following restrictions:

$$f(a+b) = f(a) + f(b)$$
$$cf(b) = f(cb)$$

Although both equations define the concept, a brief discussion of the first equation is of interest here. Basically, the first equation says that if one fully understands the response of component (a) and component (b), then the response of the summation of components (a + b) are determined. There are many examples of this cited in textbooks and formal courses of study. In fact, one finds them in science, engineering, management, etc. One classic example and application is the Principle of Superposition.[5] Unfortunately, the world of experience tends to quickly reveal deviations from linear behavior.

A simple way of addressing non-linearity is to acknowledge the deviation from linearity.

$$\delta + f(a+b) = f(a) + f(b)$$

Here, δ is shown as the deviation from linear behavior. Analytical solutions to non-linear problems are not as clear cut as the mathematics developed for analysis of linear systems. But such tools exist. It is not the purpose here to develop an exposition of the available analytical methods, but to give a simple but practical approach. Discrete dynamical approaches can be used that resemble the method of successive approximations.[6]

$$\delta + f(a_{n+1} + b_{n+1}) = f(a_n) + f(b_n)$$

What this expression is attempting to convey is that by first making an estimate on one side of the equation the other side can be corrected in an attempt to minimize the deviation from linearity. The iteration then continues with the hope that an "equilibrium" point is found where:

$$a_{n+1} = a_n$$
$$b_{n+1} = b_n$$

In short, solutions are not always unique if they exist at all. The result of this effort can yield results such as convergence, divergence, a limit cycle or chaotic behavior. These observations fall into a grouping known as complex behavior. This is an area of substantial interest in the mathematical and the scientific communities.

A complex system can be characterized by unique behaviors such as:[7]

Self-organizing behavior
Sensitive dependence on initial conditions
Chaos

What follows is a demonstration that a battery shows the properties of a complex system. If this is the case, the notion of arriving at a complete battery model must take a different direction than application of linear modeling techniques.

Self-organizing Behavior

Observations of the charging of a flooded lead acid battery have long revealed the general behavior shown in figure 1. [8]

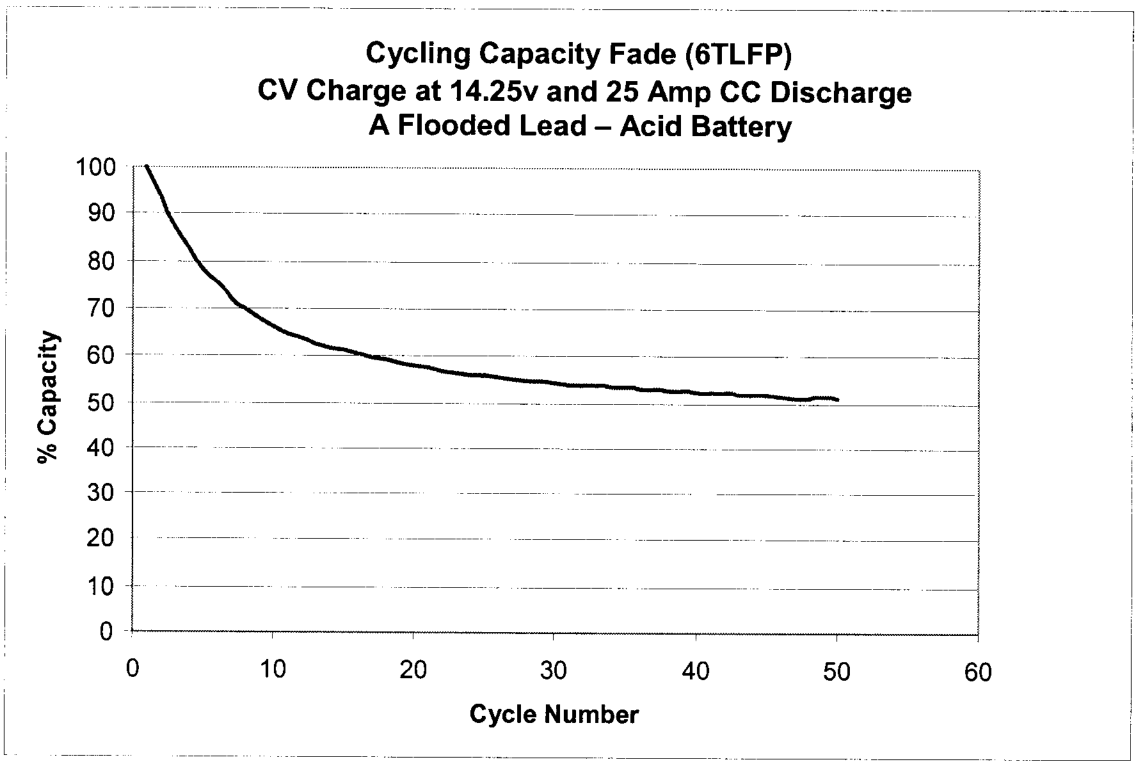

Figure 1. Successive cycle behavior of a flooded lead acid battery.

This figure shows the observed loss of capacity that is attributed to the phenomenon known as electrolyte stratification. In short, as the battery is charged, concentrated sulfuric acid is produced at the electrodes. The concentrated acid has a density of 1.8 as compared to that of the electrolyte which is about 1.2. The high density acid settles to the bottom of the cell and collects there. The loss of capacity is the consequence of the sulfuric acid being selectively removed from the top of the cell and accommodated at the

bottom of the cell. Since sulfuric acid is one of the reactants in a lead acid battery, the top of the cell is starved of one of the reactants that is in overabundance at the bottom of the cell. Figure 2 shows the effect of stirring the electrolyte by overcharging the battery so as to mix the electrolyte and restore the sulfuric acid distribution in the cells of the battery.

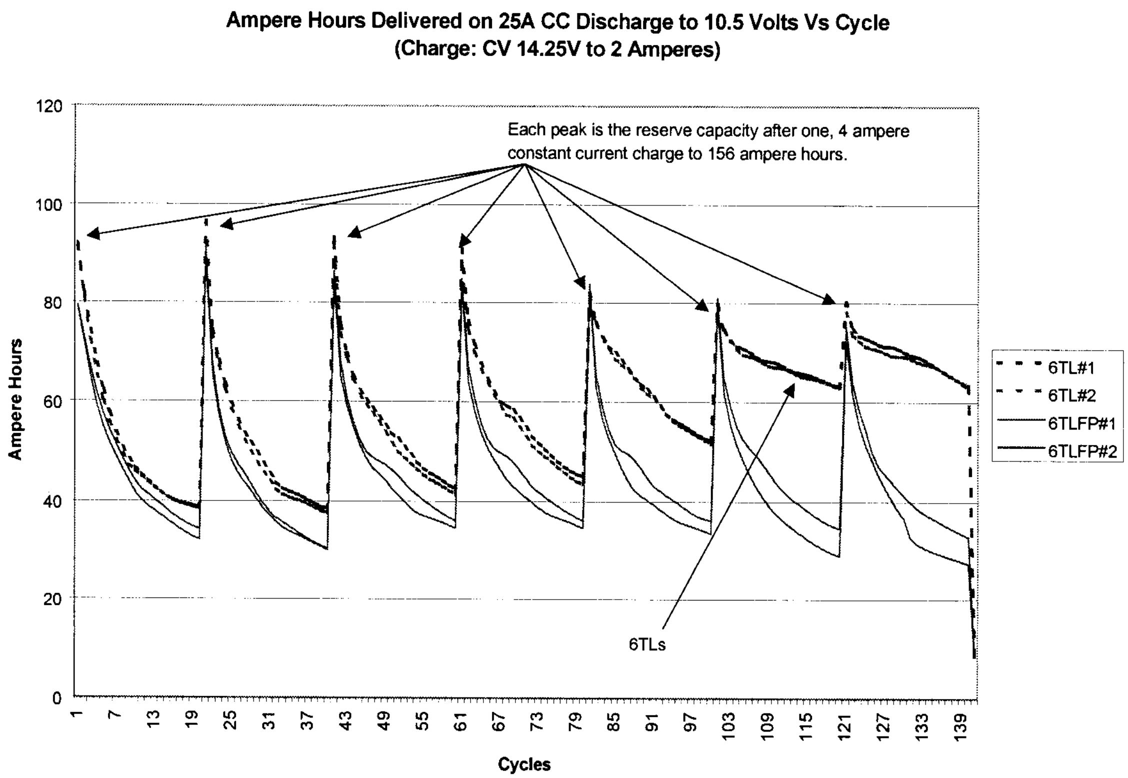

Figure 2. Effect of gassing on overcharge during the repetitive cycling of batteries. The 6TL design has an antimonial alloy positive grid. The 6TLFP has a calcium alloy positive grid.

The gassing within the cells during overcharge restores the capacity of the battery by mixing the electrolyte. The sequence is repeated to demonstrate the reproducibility of the effect. It is noteworthy that the batteries having antimonial grids eventually provide sufficient internal gassing to mix the electrolyte and in so doing, maintain a higher capacity during repetitive cycling.

The point behind raising this stratification effect is that during the cycling of a battery a concentration gradient is developed that is stabilized by gravity. Unassisted, the mixing takes place by a diffusive mass transfer which is a very slow process. The existence of the concentration gradient is a non-equilibrium condition. In effect, as a lead acid battery is cycled, a concentration gradient appears which did not exist previously. This concentration gradient constitutes an ordering of the system. With respect to the electrolyte, a decrease in Entropy has taken place. This is evidence for self-organizing behavior.

Sensitive Dependence on Initial Conditions

There was a time when the failure of lead acid batteries was characterized as due to a generic cause known as Sulfation.[8] This is actually an example of an attempt to impose linear behavior on lead acid battery degradation. In fact, Sulfation used in this way represents the name given to the set of all failure modes that a lead acid battery can experience. Continued technological development allowed the failure modes to be better identified and understood mechanistically (to a greater or lesser degree). A listing of the major failure modes is presented in Table 1.

Table 1. Listing of the lead acid battery failure modes

Major Lead Acid Battery Failure Modes

- Loss of electrolyte
- Electrolyte stratification
- Hydration
- Grid corrosion followed by detachment
- Internal shorting
- Lead oxide film formation at positive current collectors
- Agglomeration of finely divided lead at negative electrodes
- Electrolyte contamination
- External damage to case and terminals
- Hard sulfation
- Inter-cell connector failure
- VRLA unique failure modes
    - Thermal runaway
    - Lead sulfate accumulation at the negatives

There is an observation that needs to be made here to bring the notion of a failure mode within the confines of complexity theory. It is to be noted that the rate of change of any performance variable with respect to time goes to zero when a battery failure takes place. This means that these failure modes can be considered as having the property of being equilibrium points. In complexity theory, these failure modes could be identified as fixed point attractors.

It is very difficult to predict the failure mode of a new battery before it is placed in service. However, the manner of use or of testing could affect the number of likely failure modes that could influence the failure. Those failure modes that might bring about the failure are the domain of attraction. How the battery fails depends upon how it is used (and how it is built). This illustrates the effect known as sensitive dependence on initial conditions.

Chaotic Oscillations

An interesting situation occurs when one attempts to place a VRLA battery into thermal runaway.[9] A transition zone between stable operation and thermal runway exists wherein the battery goes into electrical oscillation. The effect is an interesting one. This effect appears to be the consequence of a competition between two exponentially controlled processes. The rising temperature exponentially accelerates the oxygen evolution reaction. However, the oxygen evolution process displaces the electrolyte in the interelectrode gap. This process creates an increasing IR drop that suppresses the driving voltage of the electrode reaction which is also an exponential function. The two processes involve an accelerating effect and a retarding effect. Also, since there are 6 cells in series in this battery, the interaction between the cells gives rise to this chaotic behavior. See figure 3 for a visualization of the effect.

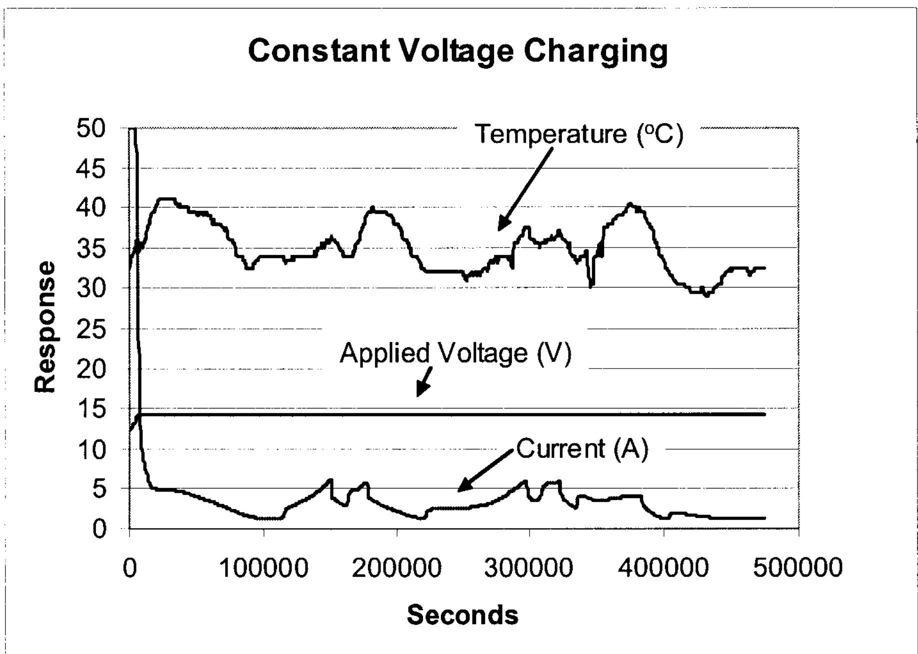

Figure 3. 120 Ah 12 V Hawker Armasafe battery in oscillation during overcharge at an applied 14.25V. The temperature was measured at the negative terminal.

This represents a demonstration of chaotic behavior that is a characteristic of a complex system.

Closing Comments

At the beginning of this paper, the observation was made that battery technology development appears to focus on discrete component development with the hope that the

integration of the new components will result in improved system performance. This has led to iterative improvements over time and significant improvements have resulted. This approach is consistent with the method for arriving at solutions for non-linear processes. The gist of this paper was to show that a battery has the characteristics of a non-linear system. It would seem reasonable to approach the modeling of a battery or an electrochemical cell as a non-linear component. Techniques are available to accomplish this that includes discrete and continuous dynamical analysis. This kind of investigatory procedure can generate some new perspectives on battery system behavior.

References

1. Bard, A.J. and L.R. Faulkner, Electrochemical Methods, John Wiley and Sons, 1980.

2. Compton, T.R., Battery Reference Book, SAE International, Second Edition, 1996, pp. 1/3-66.

3. Curley, E., The Collected Works of Spinoza, Princeton University Press, 1985, pp. 193-196.

4. Buck, R.C., Advanced Calculus, McGraw-Hill, Third Edition, 1978, p.334.

5. Hayt, W.H., and J.E. Kimmerly, Engineering Circuit Analysis, Fourth Edition, McGraw-Hill, 1986, p.74.

6. Sanderfur, J.T., Discrete Dynamical Modeling, Oxford University Press, New York, 1993.

7. Nicolis, G. and I. Prigogine, Exploring Complexity, W.H. Freeman and Co., New York, 1998, pp. 5-44.

8. Catherino, H.A., F. Feres and F. Trinidad, "Sulfation in Lead Acid Batteries," J. Power Sources, Volume 129, Issue 1, 15 April 2004. pp. 113-120.

9. Catherino, H.A., Complexity in battery systems: Thermal Runaway in VRLA batteries, J. Power Sources, 2005, (available on line on Science Direct).